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13. ABSTRACT *(Maximum 200 words)*

We have continued to optimize our processing to reduce the oxygen and metallic impurities present in the AlN samples. Texture analysis of the hot pressed nanocrystalline AlN powders shows that a high degree of alignment has been achieved with respect to the (002) direction. The piezoelectric properties of these samples should be investigated further to determine their piezoelectric efficiency. Additional studies on the surface chemistry of the nanocrystalline AlN were undertaken through the use of photoacoustic Fourier-transform infrared spectroscopy. Through this technique we were able to observe the surface species present initially and as the AlN decomposed during exposure to the laboratory air.

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"Processing of Nanocrystalline Nitrides and Oxide Composites"

Technical Report on ONR Grant No. N00014-95-1-0626
for the period of January 1, 1999 - March 31, 1999

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Nanocrystalline Aluminum Nitride

Sintering Results

Research on improving and optimizing the processing of the nanocrystalline AlN powder to produce high purity and fully dense pressurelessly sintered parts has continued. Various sources of contaminants, including die lubricants and crucible outgassing, have been identified and corrected to reduce both metallic and oxygen impurities in the sintered parts. We have begun to use a high purity boron nitride (BN) powder as a die lubricant both for pellet forming and as a barrier layer between the AlN and the graphite die during hot pressing. This should reduce the carbon contamination previously reported in hot pressed nanocrystalline AlN samples. These efforts at identifying and removing contamination sources will continue since a small amount of an unidentified phase is still detectable by X-ray diffraction in the samples after sintering.

In a previous report, the synthesis of nearly fully dense textured AlN produced by hot-pressing of nanocrystalline AlN powder was described. The texturing may be interesting since AlN can be used as a piezoelectric material at higher temperatures than other common piezoelectric materials. Since the forming method (hot pressing) is radially symmetric, a pole figure analysis of the texturing can be simplified to a plot of the average intensity of the (002) peak versus the tilt angle of the specimen. The profile of the X-rays incident on the surface of the sample is a function of the tilt angle, and the reflection intensity is a function of the density of the sample. Therefore, the easiest way to illustrate the alignment of the textured specimens is to ratio the intensity of the (002) peak at a given tilt with that of an untextured sample (Figure 1). In the case of a single crystal, the peak ratio would be nearly zero until very high tilt angles where it would approach infinity. Obviously, we have not achieved perfect alignment for the AlN; however, we have obtained a higher degree of alignment than other researchers have achieved using similar bulk powder processing methods. It would therefore be interesting to investigate the piezoelectric properties of this textured polycrystalline AlN in the future.

Surface Characterization

In addition to the sintering and thermal conductivity studies currently underway, the surface chemistry of the nanocrystalline aluminum nitride powder has also been investigated by photoacoustic Fourier-transform infrared (PA-FTIR) spectroscopy. A Bio-Rad FTS-60A with a photoacoustic cell and capable of scanning between 400 and 4000 cm^{-1} was used for the analysis. The FTIR spectra shown in Figure 2 were collected for powders that had been unexposed, or had been exposed for various amounts of time to the air in the laboratory environment. For figure 2(a) the powder was loaded into the photoacoustic cell inside the glovebox, sealed, and then analyzed shortly thereafter to avoid exposure to the atmosphere. This spectra is very similar to that reported by Merle-Méjean et al. for AlN that had been in-situ heated to 500°C under vacuum prior to analysis [1]. Unfortunately, the experimental mode that they used (transmission FTIR) precluded analysis below 1000 cm^{-1} due to strong phonon vibrations so that we cannot compare the lattice vibrations of our samples to their system. For the unexposed powder, the double peak at 725 and 840 cm^{-1} is due to Al-N lattice vibrations and the small peak at 1560 cm^{-1} is assigned to NH_2 vibrations. The sharp peaks at 2010 and 2085 cm^{-1} are probably due to adsorbed CN or HCN, which can be formed in low concentrations when the hot graphite crucible reacts with the ammonia gas in the forced flow reactor. The very small peaks at 2160 and 2260 cm^{-1} are reportedly due to Al-H bonds either within the AlN or on the surface, respectively [1]. The broad peak centered at 3200 cm^{-1} is due to NH surface species. There does appear to be a small OH signal (with Al in octahedral location) in the unexposed sample as shown by the small peak at 3740 cm^{-1} [1].

As the sample undergoes hydrolysis during exposure to air, a number of peaks disappear and some additional peaks, primarily associated with OH, appear. After only 5 minutes of exposure to the atmosphere, the peaks at 2010 and 2085 cm^{-1} are reduced significantly as the CN or HCN species desorb or react with water in the environment. The broad peak of physisorbed or weakly chemisorbed water at 3400 cm^{-1} [1] also emerges with exposure to air. In addition, the Al-N lattice peaks lose intensity as water reacts with the powder and consumes the AlN. The broadening of the lattice peaks and the appearance of a shoulder at 550 cm^{-1} are due to Al-O lattice vibrations [2] as the AlN surface is converted to AlOOH. The NH_2 peak at 1560 cm^{-1} is eventually dominated by the water bending mode at 1645 cm^{-1} and the $CO_3^{=}$ vibrations at 1530 cm^{-1} and 1395 cm^{-1} [2]. It is evident that even a five-minute exposure, such as the powders might experience on removal from a powder collection device or on loading into a furnace, can have a large effect on the surface chemistry of these nanocrystalline powders. These results highlight the importance of maintaining an oxygen-free and moisture-free environment during the synthesis and processing of nanocrystalline AlN.

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[1] T. Merle-Méjean, M.-I. Baraton, P. Quintard, Y. Laurent, and V. Lorenzelli, "Fourier-transform Infrared Characterization of an Aluminum Nitride Surface," *J. Chem. Soc. Faraday Trans.*, **89** [16] 3111-15 (1993).

[2] J.B. Benziger, S.J. McGovern, and B.S.H. Royce, "IR Photoacoustic Spectroscopy of Silica and Aluminum Oxide," pp. 448-463 in Catalyst Characterization Science, edited by M.L. Deviney and J.L. Gland, ACS Symposium Series No. 288, American Chemical Society, 1985.

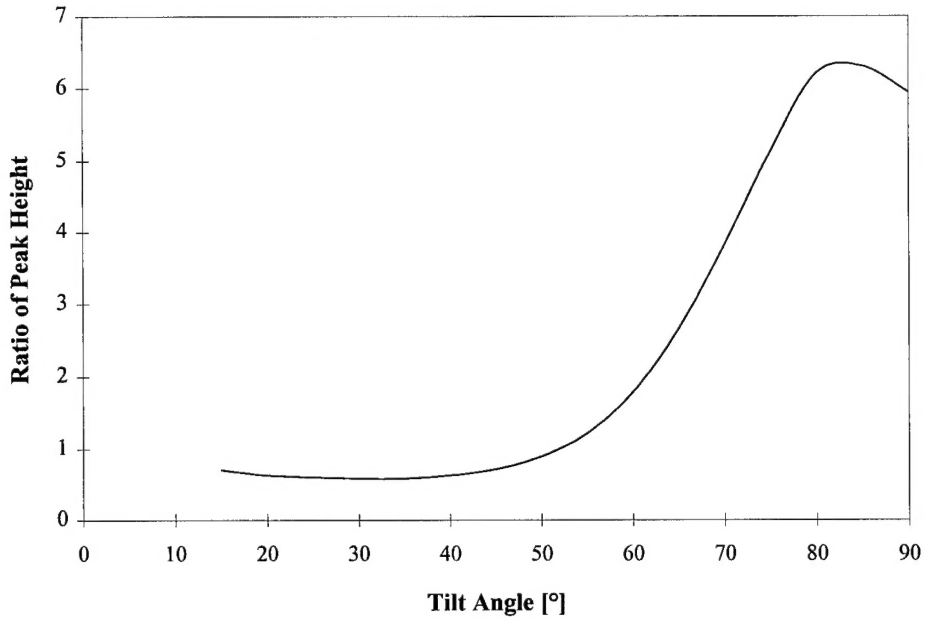

Figure 1. Peak height of the (002) diffraction plane of nanocrystalline hot pressed AlN divided by the peak height of a randomly oriented powder sample plotted as a function of tilt angle.

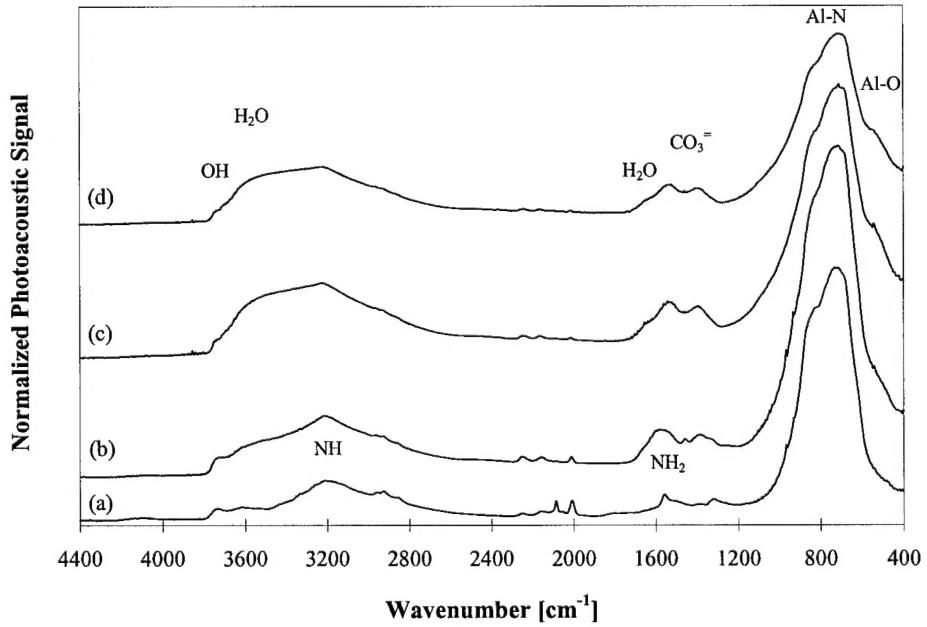

Figure 2. PA-FTIR spectra of nanocrystalline AlN (a) prior to exposure, and after exposure to air for (b) 5 minutes, (c) 12 hours, (d) and 18 hours.